$\mathcal{P},\mathcal{T}$-Odd Interactions in Atoms and Molecules

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Outline

- Relativistic many-body methods
- Atomic EDMs : Hg and Tl
- Molecular EDMs : HfF^+ and TaO^+

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- **Relativistic many-body methods**
- Atomic EDMs : Hg and Tl
- Molecular EDMs : HfF^+ and TaO^+

Atomic and Molecular Correlated Wavefunctions

- Solve relativistic equation of motion (yields wavefunctions)

- Dirac-Coulomb Hamiltonian operator (molecules)

$$\hat{H}^{DC} = \sum_i^n \left[c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + \sum_A^N \frac{Z}{r_{iA}} \mathbb{1}_4 \right] + \sum_{i,j>i}^n \frac{1}{r_{ij}} \mathbb{1}_4 + \sum_{A,B>A}^N V_{AB}$$

- Dirac-Coulomb-Gaunt Hamiltonian operator (molecules)

$$\hat{H}^{DCG} = \sum_i^n \left[c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + \sum_A^N \frac{Z}{r_{iA}} \mathbb{1}_4 \right] + \sum_{i,j>i}^n \left(\frac{1}{r_{ij}} \mathbb{1}_4 - \tfrac{1}{2} \frac{\vec{\alpha}_i \vec{\alpha}_j}{r_{ij}} \right) + \sum_{A,B>A}^N V_{AB}$$

- Dirac-Coulomb Hamiltonian + external electric field (atoms)

$$\hat{H}^{\text{Dirac-Coulomb}} + \hat{H}^{\text{Int-Dipole}} = \sum_i^n \left[c\,\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + \frac{Z}{r_i} \mathbb{1}_4 \right] + \sum_{i,j>j}^n \frac{1}{r_{ij}} \mathbb{1}_4 + \sum_i^n \mathbf{r}_i \cdot \mathbf{E}_{\text{ext}}\, \mathbb{1}_4$$

Atomic and Molecular Correlated Wavefunction

- All-electron Dirac-Coulomb Hartree-Fock (DC(G)HF) calculation
  set of time-reversal paired 4-spinors $\hat{K}\varphi_i = \varphi_{\bar{i}}$ and $\hat{K}\varphi_{\bar{i}} = -\varphi_i$

$$\hat{K}(n) := e^{-\frac{i}{2}\pi\left(\sum_{j=1}^{n} \boldsymbol{\sigma}\otimes\mathbb{1}_2(j)\right)\cdot\vec{e}_y} \prod_{j=1}^{n} \hat{K}_0(j)$$

- Expansion and variation[1] in n-electron sector of Fock space

$$|\psi_k\rangle = \sum_{I=1}^{\dim\mathcal{F}^{\mathrm{t}}(\mathrm{M},\mathrm{n})} c_{kI}\,(\mathcal{S}\overline{\mathcal{T}})_I\,|\;\rangle$$

unbarred (Kramers up) string $\mathcal{S} = a_i^\dagger a_j^\dagger a_k^\dagger \ldots$

barred (Kramers down) string $\overline{\mathcal{S}} = a_{\bar{l}}^\dagger a_{\bar{m}}^\dagger a_{\bar{n}}^\dagger \ldots$

Linear expansion: **Configuration Interaction**

Exponential expansion: Coupled Cluster

[1] S. Knecht, H.J.Aa. Jensen, T.F., *J Chem Phys* **132** (2010) *014108*

$\mathcal{P}$,$\mathcal{T}$-odd Property Calculations

using correlated wavefunctions

Expectation values over relativistic Configuration Interaction wavefunctions[2]

$$\left\langle \hat{H}' \right\rangle_{\psi_k^{(0)}} = \sum_{I,J=1}^{\dim\mathcal{F}^{\mathrm{t}}(\mathrm{M,n})} c_{kI}^* c_{kJ} \left\langle \, | \, (\mathcal{S}\overline{\mathcal{T}})_I^\dagger \left| \hat{H}' \right| (\mathcal{S}\overline{\mathcal{T}})_J \, | \, \right\rangle$$

Property operator in basis of Kramers-paired molecular spinors

$$\hat{H}' = \sum_{p,q=1}^{P_u} h'_{pq} \, a_p^\dagger a_q + \sum_{p=1}^{P_u} \sum_{q=P_u+1}^{P} h'_{p\overline{q}} \, a_p^\dagger a_{\overline{q}} + \sum_{p=P_u+1}^{P} \sum_{q=1}^{P_u} h'_{\overline{p}q} \, a_{\overline{p}}^\dagger a_q + \sum_{p,q=P_u+1}^{P} h'_{\overline{p}\overline{q}} \, a_{\overline{p}}^\dagger a_{\overline{q}}$$

First-term contribution to expectation value

$$W'(\Psi_k)_1 = \sum_{I,J=1}^{\dim\mathcal{F}^{\mathrm{t}}(\mathrm{P,N})} c_{kI}^* c_{kJ} \sum_{m,n=1}^{P_u} h_{mn}^M$$
$$\left\langle \, | \, \prod_{p=1}^{N_p\in\mathcal{S}_I} \prod_{\overline{p}=N_p+1}^{N_p\in\mathcal{S}_I+N_{\overline{p}}\in\overline{\mathcal{T}}_I} a_{\overline{p}} a_p \, a_m^\dagger a_n \prod_{q=1}^{N_p\in\mathcal{S}_J} \prod_{\overline{q}=N_p+1}^{N_p\in\mathcal{S}_J+N_{\overline{p}}\in\overline{\mathcal{T}}_J} a_q^\dagger a_{\overline{q}}^\dagger \, | \, \right\rangle$$

[2] S. Knecht, Dissertation, HHU Düsseldorf 2009

Generalized Active Spaces

Parameterization of the correlated wavefunction

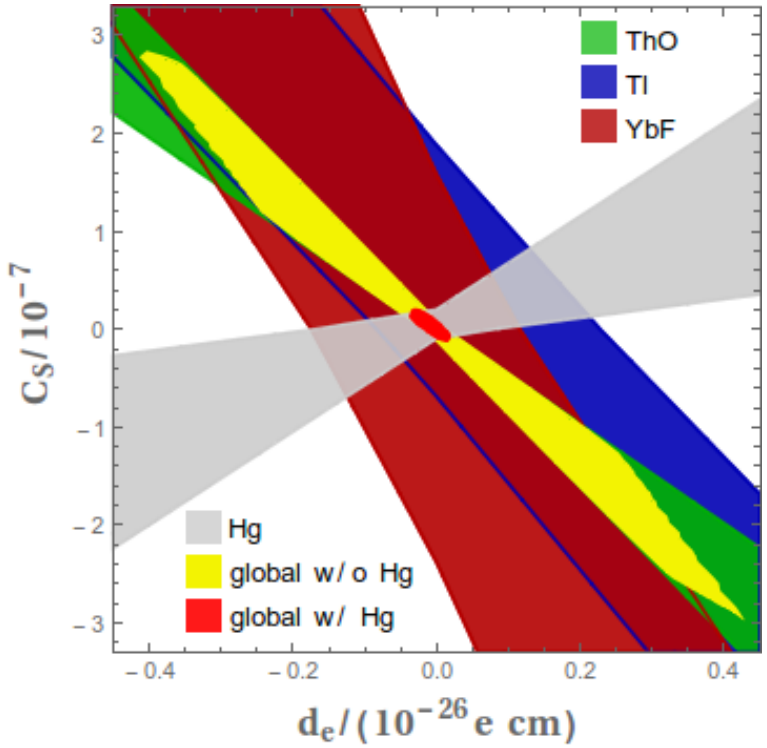
	# of Kramers pairs	accumulated # of electrons min.	max.
Virtual	81	20	20
Hg: 6p 7s 7p 6d 8p 8s 9p 9s 10p 10s	24	20−p	20
Hg: 6s 5d	6	20−(m+n)	20
Hg : 5s 5p	4	8−m	8
Frozen core	(34)		

Best model:
m=1,n=2,p=2

Outline

- Relativistic many-body methods
- **Atomic EDMs : Hg and Tl**
- Molecular EDMs : HfF^+ and TaO^+

More Stringent Bounds[3]



$$\Delta E_{\mathcal{P},\mathcal{T}} = -\langle \mathbf{d}_{\text{sys}} \cdot \mathbf{E}_{\text{ext}} \rangle = \frac{1}{2} \left(\alpha_{d_e} d_e + \alpha_{C_S} C_S \right) \langle \mathbf{n} \cdot \mathbf{z} \rangle \left(E_{\text{ext}} \right)$$

Combination with other systems (measurements/calculations)[5]

- Diamagnetic systems (probably) give rise to "orthogonal" constraints[4]
  $\alpha_{d_e}(\text{Hg}) > 0 \qquad \alpha_{C_S}(\text{Hg}) < 0$
- Yields much more stringent bounds on $\mathcal{CP}$-violating parameters

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[3] "Seed Money" Project 2016, M. Jung (Munich), TF

[4] A. M. Mårtensson-Pendrill and P. Öster, *Phys. Scr.* **36** (1987) *444*

[5] M. Jung, A. Pich *J. High En. Phys.* **5** (2014) *076*

Hg EDM

Motivation from BSM scenarios[6]

BSM Model	Relative importance of $\mathcal{P}$,$\mathcal{T}$-odd interactions
multi Higgs	$V_S \approx 5V_P$ $V_T = 0$
vector/scalar leptoquark	$V_S \approx 5V_P$ $V_T = 0$

- In multi-Higgs BSM V_S and effect due to electron EDM can be equally important
- $\Rightarrow$ Direct calculation of α_{C_S} is of interest

[6] S. M. Barr, *Phys. Rev. D* **45** (1992) *4148*

EDMs in paramagnetic atoms:

Nucleon-electron SPS interaction

- Effective interaction Hamiltonian

  $$\hat{H}_{\text{ne-SPS}}(S) = \frac{\imath G_F}{\sqrt{2}} A C_S \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e)$$

- To first order in perturbation theory

  $$(\Delta\varepsilon)_J = \left\langle \imath \frac{G_F}{\sqrt{2}} A C_S \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \right\rangle_{\psi_J^{(1)}}$$

  ψ_J: atomic many-particle state

- Atomic EDM is defined as

  $$d_a = - \lim_{E_{\text{ext}} \to 0} \left[\frac{\partial(\Delta\varepsilon)}{\partial E_{\text{ext}}} \right]$$

- Definition of an ne-SPS ratio

  $$S := \frac{d_a}{A C_S \frac{G_F}{\sqrt{2}}}$$

- from which follows

  $$S = - \lim_{E_{\text{ext}} \to 0} \left[\frac{\partial}{\partial E_{\text{ext}}} \left\langle \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \right\rangle_{\psi_J^{(1)}(E_{\text{ext}})} \right]$$

$\mathcal{P},\mathcal{T}$-odd Effects in Closed-Shell States ?

- Atomic electronic state in $E_{\rm ext} \neq 0$:
  $|M_J\rangle$
- In the closed-shell subcase ($p_{1/2}^2 \neq$ closed shell) it follows:
  $|M_S = 0\rangle$
- Then it is straightfoward to show that
  $\langle M_S = 0| \sum\limits_j \gamma^0(j)\, \Sigma_3(j)\, E_3\, |M_S = 0\rangle = 0$ and
  $\langle M_S = 0| \sum\limits_j \gamma^0(j)\, \Sigma_\pm(j)\, E_\pm\, |M_S = 0\rangle = 0$
- The electron EDM Hamiltonian can be reformulated as
  $$-\left\langle \sum_{j=1}^{n} \gamma_j^0\, \mathbf{\Sigma}_j \cdot \mathbf{E}_j \right\rangle_{\psi^{(0)}} \approx \frac{2\imath c}{e\hbar} \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \vec{p}_j{}^{\,2} \right\rangle_{\psi^{(0)}}$$
- which has the same transformation properties as the ne-SPS Hamiltonian.
- No $\mathcal{P},\mathcal{T}$-odd effects in closed-shell states (in $E_{\rm ext} \neq 0$).

Magnetic-Hyperfine Perturbed (Atomic) States

- Basis: CI eigenstates $\left\{\left|\psi_K^{(0)}\right\rangle\right\}$ of
  $\hat{H}^{(0)} := \hat{H}^{\text{Dirac-Coulomb}} + \sum_j \hat{\mathbf{r}}_j \cdot \mathbf{E}_{\text{ext}}\, \mathbb{1}_4$

- We take the hyperfine-perturbed electronic wavefunction to first order:
  $\left|\psi_J^{(1)}\right\rangle = \left|\psi_J^{(0)}\right\rangle + \sum_{K\neq J} \frac{\left\langle\psi_K^{(0)}\right|\hat{H}_{\text{HF}}^{(1)}\left|\psi_J^{(0)}\right\rangle}{\varepsilon_J^{(0)}-\varepsilon_K^{(0)}} \left|\psi_K^{(0)}\right\rangle$

- where for nucleus A in atomic units:[7]
  $\hat{H}_{\text{HF}}^{(1)} = \frac{g\, m_e}{2c\, I\, m_p} \sum_{k=1}^{3} \sum_{i=1}^{n} \left(\frac{\boldsymbol{\alpha}_i \times \boldsymbol{r}_{iA}}{r_{iA}^3}\right)_k$
  g: nuclear g-factor for isotope ${}^A X$
  I: nuclear spin quantum number

- In the following, we exploit rotational invariance:
  $\hat{R}_{\text{SU(2)}}^\dagger\, \imath\gamma^0\gamma^5 \boldsymbol{p}^2(\rho(\boldsymbol{r}))\, \hat{R}_{\text{SU(2)}} = \imath\gamma^0\gamma^5 \boldsymbol{p}^2(\rho(\boldsymbol{r}))$ with
  $\hat{R}_{\text{SU(2)}} = e^{\imath\boldsymbol{\Theta}\cdot(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}})}$

[7] TF and M.K. Nayak, *J. Mol. Spectrosc.* **300** (2014) *16*

Atomic EDMs

The first direct calculation[8] of α_{C_S} for a **diamagnetic atom**

$$S := -\frac{\left\langle \imath \sum\limits_j \gamma_j^0 \gamma_j^5 \rho_N(\mathbf{r}_j) \right\rangle_\Psi}{E_{\text{ext}}} \qquad \alpha_{C_S} = S\, A\, \frac{G_F}{\sqrt{2}}$$

$$\begin{aligned}
W_c &= \frac{1}{\left\langle \psi_J^{(1)} \middle| \psi_J^{(1)} \right\rangle} \left\langle \psi_J^{(1)} \middle| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}e) \middle| \psi_J^{(1)} \right\rangle \\
&= \frac{1}{\left\langle \psi_J^{(1)} \middle| \psi_J^{(1)} \right\rangle} \left[\left\langle \psi_J^{(0)} \middle| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}e) \middle| \psi_J^{(0)} \right\rangle \right. \\
&\quad + \sum_{K \neq J} \frac{\left\langle \psi_K^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_J^{(0)} \right\rangle}{\varepsilon_J^{(0)} - \varepsilon_K^{(0)}} \left\langle \psi_J^{(0)} \middle| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}e) \middle| \psi_K^{(0)} \right\rangle \\
&\quad + \sum_{K \neq J} \frac{\left\langle \psi_J^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_K^{(0)} \right\rangle}{\varepsilon_J^{(0)} - \varepsilon_K^{(0)}} \left\langle \psi_K^{(0)} \middle| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}e) \middle| \psi_J^{(0)} \right\rangle \\
&\quad \left. + \sum_{K,L \neq J} \frac{\left\langle \psi_K^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_J^{(0)} \right\rangle \left\langle \psi_J^{(0)} \middle| \hat{H}_{\text{HF}}^{(1)} \middle| \psi_L^{(0)} \right\rangle}{\left(\varepsilon_J^{(0)} - \varepsilon_K^{(0)}\right)\left(\varepsilon_J^{(0)} - \varepsilon_L^{(0)}\right)} \left\langle \psi_L^{(0)} \middle| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}e) \middle| \psi_K^{(0)} \right\rangle \right]
\end{aligned}$$

[8] TF, unpublished work.

Atomic EDMs

Hg excited-state energies

ψ model : cvTZ/6p7s7p6d8p8s9p9s10p10sSDT12_SD12_50au

Excited state	configuration	theory $[\mathrm{cm}^{-1}]$	experiment[9] $[\mathrm{cm}^{-1}]$
$\boldsymbol{^3P_0}$	$\boldsymbol{5d^{10}6s6p}$	**36229**	**37645**
$^3P_1$	$5d^{10}6s6p$	38050	39412
$^3P_2$	$5d^{10}6s6p$	42619	44043
$^1P_1$	$5d^{10}6s6p$	54299	54069
$\boldsymbol{^3S_1}$	$\boldsymbol{5d^{10}6s7s}$	**67310**	**62350**
...	...	...	...
$\boldsymbol{^3P_0}$	$\boldsymbol{5d^{10}6s7p}$	74279	**69517**
...	...	...	...
$\boldsymbol{^3P_0}$	$\boldsymbol{5d^{10}6s8p}$		**76447**

Mean deviation: $\approx 6.2\%$

[9] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD team *NIST Atomic Spectra Database* (2015) *173001*

Atomic EDMs

Hg excited-state energies

- Symmetry interplay in ME product:
  $\left\langle \psi_k^{(0)} \right| \hat{H}_{\mathsf{HF}}^{(1)} \left| \psi_j^{(0)} \right\rangle \left\langle \psi_j^{(0)} \right| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \left| \psi_k^{(0)} \right\rangle$

- $^3\boldsymbol{P_0}$ and $M_J = 0$ components of $^3\boldsymbol{S_1}$ strongest contributors

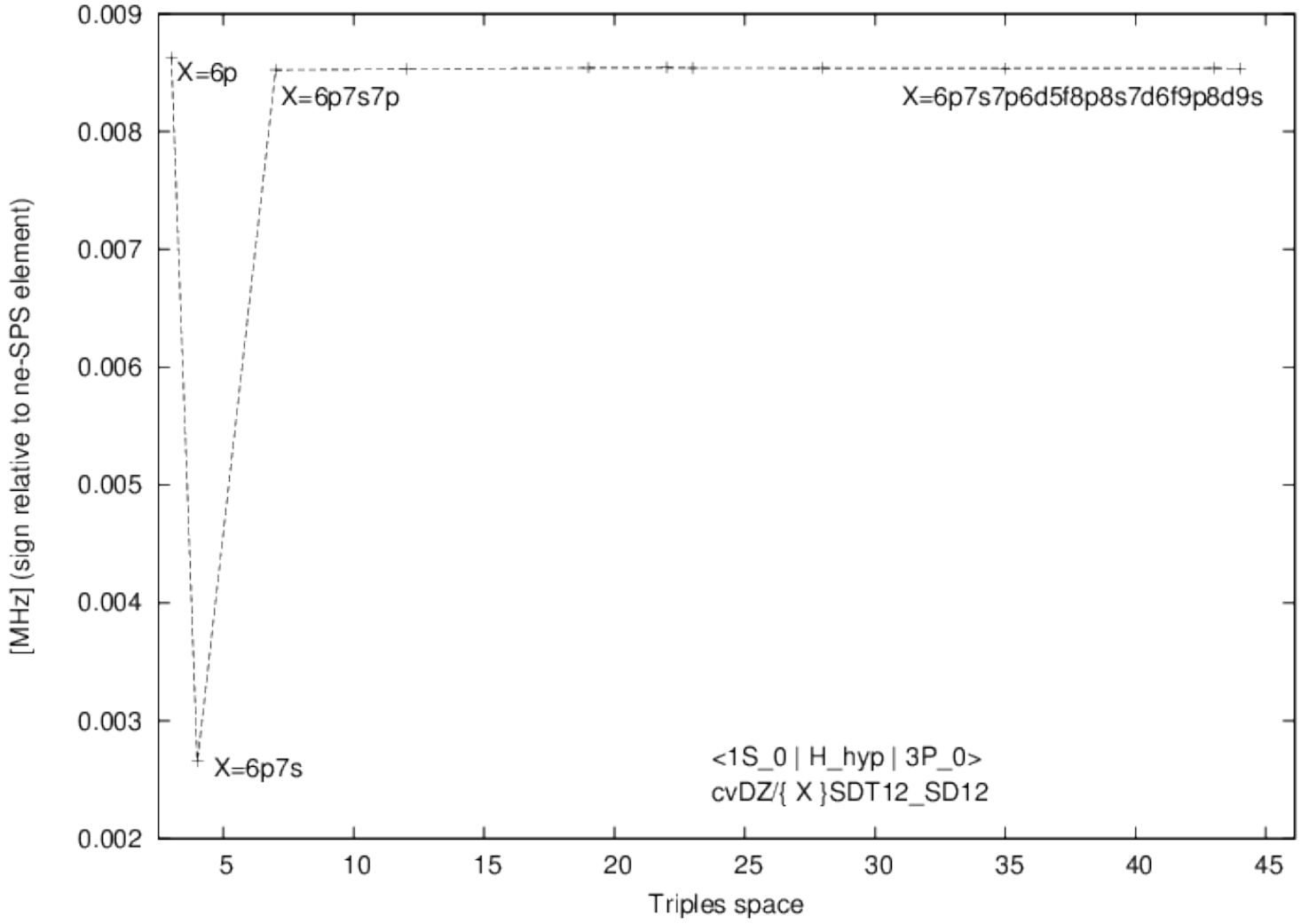
  Scenario 1: $\left\langle \psi_k^{(0)} \right| \hat{H}_{\mathsf{HF}}^{(1)} \left| \psi_j^{(0)} \right\rangle$ large, $\left\langle \psi_j^{(0)} \right| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \left| \psi_k^{(0)} \right\rangle$ small

  $^3\boldsymbol{S_1}$ contribution

  Scenario 2: $\left\langle \psi_k^{(0)} \right| \hat{H}_{\mathsf{HF}}^{(1)} \left| \psi_j^{(0)} \right\rangle$ small, $\left\langle \psi_j^{(0)} \right| \imath \sum_e \gamma_e^0 \gamma_e^5 \rho(\mathbf{r}_e) \left| \psi_k^{(0)} \right\rangle$ large

  $^3\boldsymbol{P_0}$ contribution

Atomic off-diagonal Hyperfine MEs



Atomic EDMs

Hg ne-SPS ratio via magnetic hyperfine interaction

Basis/cutoff	# $M_J = 0$/# el./X	M. d. [%]	W_c [10^{-6} *a.u.*]	S [10^{-2} *a.u.*]	α_{C_S} [$10^{-22}\, e$ cm]
DZ/150 au.	4/12/6p. . .7d		7.88	−3.26	−5.39
DZ/150 au.	16/12/6p. . .7d		5.55	−2.31	−3.82
TZ/50 au.	4/12/6p7s	8.4	−9.46	3.94	6.53
TZ/50 au.	6/12/6p7s7p	6.1	−2.45	1.02	1.69
TZ/50 au.	12/12/6p7s7p	6.1	5.01	−2.09	−3.46
TZ/50 au.	12/20/6p7s7p		5.1	−2.1	−3.5
TZ/50 au.	12/12/6p. . .8s	5.4	5.3	−2.2	−3.7
TZ/50 au.	29/12/6p. . .10s	6.2	5.3	−2.2	−3.7

- Among > 100 singly-excited states ($M_J = 0$) one more non-negligible contribution:
  $\boldsymbol{^3P_0(5d^{10}6s8p)}$
- Trend: α_{C_S} will drop on the absolute

ne-SPS Interaction Ratio in Hg

Method	Ref.	$\alpha_{C_S}[10^{-22}e\,\mathrm{cm}]$
CI+MBPT	[dzuba_flambaum[10]]	(-5.1)
MCDHF	[Radziute[11]]	(-5.5)
PRCC	[Latha[12]]	(-4.3)
$\mathrm{CCSD_pT(+)}$	[Singh[13]]	(-4.4)
$\mathrm{CCSD_pT(+)}$	[B. K. Sahoo[14]]	(-3.2)
Chupp *et al.*[15] (est.)		(-5.9)
Engel *et al.*[16] (est.)		(-8.12)
This work		-3.7

Rough estimate for high-lying state: $+1.7\,[10^{-22}e\,\mathrm{cm}]$ (uncertainty 50%)

Current result $\alpha_{C_S} =$ **-2.0** $[10^{-22}e\,\mathrm{cm}]$, uncertainty of 35%

[10] *Phys. Rev. A* **80** (2009) *032120*
[11] *Phys. Rev. A* **90** (2014) *012528*
[12] *Phys. Rev. Lett.* **103** (2009) *083001*
[13] *Phys. Rev. A* **91** (2015) *030501*
[14] (2016)
[15] *Phys. Rev. C* **91** (2015) *035502*
[16] *Prog. Part. Nuc. Phys.* **71** (2013) *21*

TI EDM

Leading contributions to **EDM** of a **paramagnetic atom**

$$d_a = R\, d_e + \alpha_{C_S}\, C_S \qquad \alpha_{C_S} = S\, A\, \frac{G_F}{\sqrt{2}}$$

Enhancement factor and S ratio:

$$R := \frac{\left\langle \sum_j \gamma_j^0\, \boldsymbol{\Sigma}_j \cdot \mathbf{E}_j \right\rangle_\Psi}{E_{\text{ext}}} \qquad S := -\frac{\left\langle \imath \sum_j \gamma_j^0\, \gamma_j^5\, \rho_N(\mathbf{r}_j) \right\rangle_\Psi}{E_{\text{ext}}}$$

Model for **TI atom**	R	S [a.u.]
vDZ/SD18_CAS_3in4_SDT21/10au	-473	-331
vDZ/SD18_CAS_3in4_SDT21/20au	-479	-335
vDZ/SD8_SDT10_CAS_3in4_SDT21/10au	-471	-331
vDZ/SD10_SDT8_CAS3in4_SDTQ21/10au	≈ -480	
vDZ/SD18_CAS_3in4_SDTQ21/10au	-469	-329
vTZ/SD18_CAS_3in4_SDT21/10au	-542	-383
vTZ/SD18_CAS_3in4_SDT21/20au	-541	-383
vQZ/SD18_CAS_3in4_SDT21/10au	-555	-391
Literature values		
Porsev *et al.*, *Phys. Rev. Lett.* **108** (2012) *173001*	-573	-411
Nataraj *et al.*, *Phys. Rev. Lett.* **106** (2011) *200403*	-470	
Dzuba *et al.*, *Phys. Rev. A* **80** (2009) *062509*	-582	
Liu *et al.*, *Phys. Rev. A* **45** (1992) *R4210*	-585	

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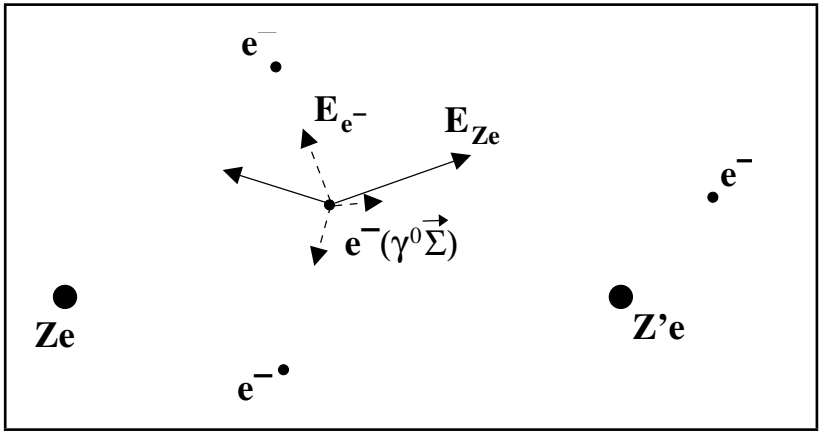
- Atomic EDMs : Hg and Tl
- **Molecular EDMs : HfF^+ and TaO^+**

Electron EDM Interaction

$$d_e = \frac{\Delta\epsilon}{E_{\rm eff}} \quad \begin{matrix}\text{(Experiment)}\\ \text{(Theory)}\end{matrix}$$



Single-particle $\mathcal{P}$- and $\mathcal{T}$-odd eEDM Hamiltonian[17]:

$$\hat{H}_{\rm EDM} = -\frac{d_e}{4}\gamma^0\gamma^5\left(\gamma^\mu\gamma^\nu - \gamma^\nu\gamma^\mu\right)F_{\mu\nu} = -d_e\gamma^0\left[\boldsymbol{\Sigma}\cdot\mathbf{E} + \imath\boldsymbol{\alpha}\cdot\mathbf{B}\right]$$

Internal electric field contributions

$$\mathbf{E}_{\rm int}(i) = \sum_{A=1}^{N}\frac{Ze\,(\vec{r}_i - \vec{r}_A)}{||\vec{r}_i - \vec{r}_A||^3} - \sum_{j=1}^{n}\frac{e\,(\vec{r}_i - \vec{r}_j)}{||\vec{r}_i - \vec{r}_j||^3}$$

Expectation value in many-body system in accord with stratagem II[18]

$$-\left\langle\sum_{j=1}^{n}\gamma_j^0\,\boldsymbol{\Sigma}_j\cdot\mathbf{E}_j\right\rangle_{\psi(0)} \approx \frac{2\imath c}{e\hbar}\left\langle\sum_{j=1}^{n}\gamma_j^0\gamma_j^5\,\vec{p}_j{}^2\right\rangle_{\psi(0)} := E_{\rm eff}$$

[17] E. Salpeter, *Phys Rev* **112** (1958) *1642*

[18] E. Lindroth, E. Lynn, P.G.H. Sandars, *J Phys B: At Mol Opt Phys* **22** (1989) *559*

$\mathcal{P}$,$\mathcal{T}$-odd Properties as Expectation Values

Interaction constants for n-electron system

- Electron eEDM interaction constant

$$W_d := \frac{2\imath c}{\Omega\, e\hbar} \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \vec{p}_j{}^{\,2} \right\rangle_{\psi_k^{(0)}} \qquad \left\langle \hat{H}_{\text{eEDM}} \right\rangle = d_e\, \Omega\, W_d$$

- S-PS nucleon-electron interaction constant

$$W_{\mathcal{S}} := \frac{\imath}{\Omega} \frac{G_F}{\sqrt{2}} A \left\langle \sum_{j=1}^{n} \gamma_j^0 \gamma_j^5\, \rho_N(\vec{r}_j) \right\rangle_{\psi_k^{(0)}} \qquad \left\langle \hat{H}_{\text{en-S-PS}} \right\rangle = k_s\, \Omega\, W_{\mathcal{S}}$$

- Nuclear magnetic quadrupole - electronic magnetic field interaction

$$W_M = \frac{3}{2\Omega} \left\langle \sum_{j=1}^{n} \left(\frac{\boldsymbol{\alpha}_j \times \mathbf{r}_{jA}}{r_{jA}^5} \right)_z (r_{jA})_z \right\rangle_{\psi_k^{(0)}}$$

HfF^+ Electronic Structure and EDM Interaction Constant

GAS-CI definitions

- Basis: uncontracted vTZ
  Hf: $\{30s, 24p, 15d, 10f, 3g, 1h\}$
  F: $\{10s, 5p, 2d, 1f\}$
- Dirac-Coulomb Hamiltonian
- Full $(SS|**)$ integrals (EDM)

	# of Kramers pairs	accumulated # of electrons min.	max.
Deleted	**(164)**		
Virtual	**118**	**34**	**34**
Hf: 6s, 5d	**6**	**34–p**	**34**
F: 2s, 2p	**4**	**32–(m+n)**	**32**
Hf: 5s, 5p F: 1s	**5**	**24–m**	**24**
Hf: 4f	**7**	**14–q**	**14**
Frozen core	**(23)**		

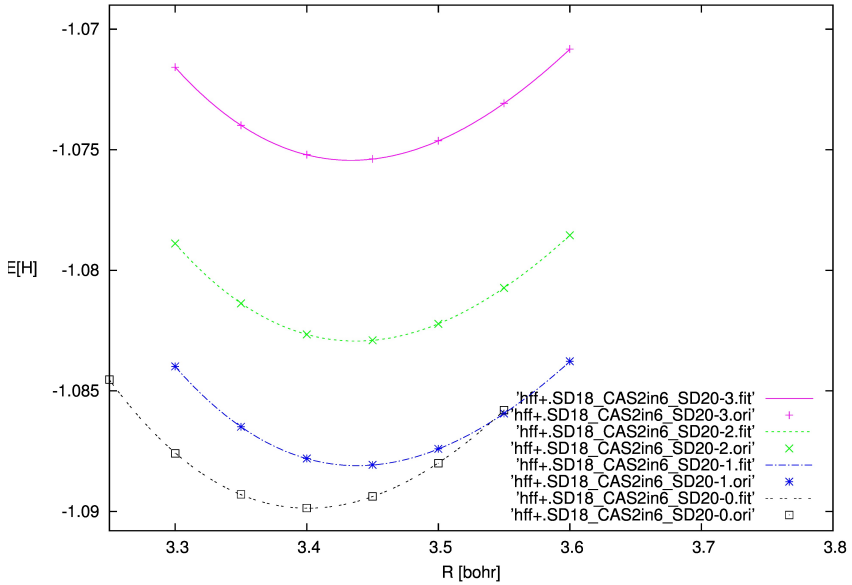
HfF^+ electronic states and spectroscopic constants

$\Omega = 3$ $(Hf^{2+}6s^15d^1)$

$\Omega = 2$ $(Hf^{2+}6s^15d^1)$

$\Omega = 1$ $(Hf^{2+}6s^15d^1)$

$\Omega = 0$ $(Hf^{2+}6s^2)$



	R_e [a.u.]				ω_e [cm^{-1}]			
Model	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$	$\Omega = 3$	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$	$\Omega = 3$
CAS-CI(10)	3.400	3.436	3.434	3.431	796	774	775	778
MR-CISD(10)	3.506	3.558	3.557	3.552	656	643	643	644
MR-CISD+T(10)	3.510	3.560			654	643		
MR-CISD(20)	3.401	3.438	3.437	3.434	800	768	769	772
Experiment[19]					790.76	760.9		
Experiment[20]	3.374	3.407			791.2	761.3	762.3	761.5

[s] K. Cossel et al., *Chem. Phys. Lett.* **546** (2012) *1*

[t] B.B. Barker, I.O. Antonov, V.E. Bondybey, M.C. Heaven, *J Chem Phys* **134** (2011) *201102*

HfF^+ spectroscopy; excitation energies

	T_e [cm^{-1}]				$T_v^{3.4[a.u.]}$ [cm^{-1}]	
Model	$\Omega = 0$	$\Omega = 1$	$\Omega = 2$	$\Omega = 3$	$\Omega = 0$	$\Omega = 1$
CAS-CI(10)	1543	0	1058	2480	1488	0
MR-CISD(10)	65	0	1007	2487	0	358
MR-CISD+T(10)	0	25			0	442
MR-CISD(20)	0	387	1521	3166	0	451
MR-CISD+T(20)					0	679
Experiment[21]	0	993	2166	3951		

- Active-space triples correction gives important contribution.
- Estimated MR-CISD+T(20) value for $T_e \approx 1180\ cm^{-1} (\Omega = 1)$
- Ongoing investigation of full PECs, transition dipole moments, and vibrational states

[21] B.B. Barker, I.O. Antonov, V.E. Bondybey, M.C. Heaven, *J Chem Phys* **134** (2011) *201102*

HfF^+: E_{eff} in the $\Omega = 1$ science state[22]

Model	$E_{\mathrm{eff}}\ \left[\frac{\mathrm{GV}}{\mathrm{cm}}\right]$
CAS-CI(10)	24.1
MR-CISD(10)	22.4
MR-CISD(20)	23.3
MR-CISD+T(20)	23.7
MR-CISD(34)	22.9
MR-CISD(34)+T	**23.3**
Estimate, Meyer et al.[23]	≈ 30
20 e^- corr., Petrov et al.[24]	24.2

(+) All-electron calculation

(+) No configuration selection

(+) Spinors as one-particle basis functions

(+) Dirac-Coulomb Hamiltonian

(-) Basis-set incompleteness
→ vQZ corrections

(-) Higher excitations
→ CC expectation values

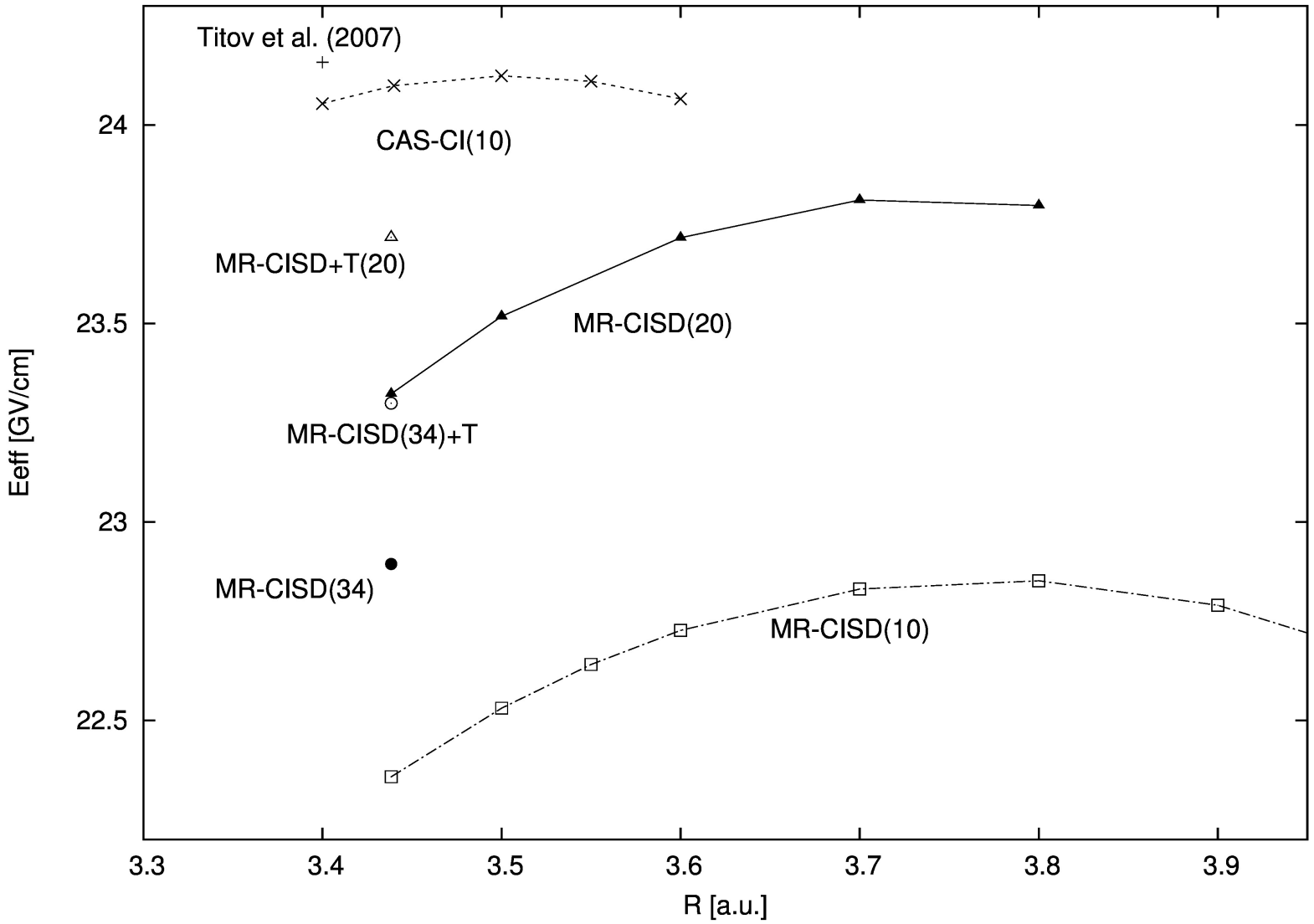
[22] T. Fleig and M. K. Nayak, *Phys Rev A* **88** (2013) *032514*

[23] E.R. Meyer, J.L. Bohn, *Phys Rev A* **78** (2008) *010502(R)*

[24] A.N. Petrov, N.S. Mosyagin, T.A. Isaev, A.V. Titov, *Phys Rev A* **76** (2007) *030501(R)*

The eEDM in a molecular framework

$\left\langle \hat{H}_{\rm edm} \right\rangle_{\psi_{\Omega=1}}$ as a function of R



HfF^+: E_{eff} in the $\Omega = 1$ science state[25]

CI Wavefunction model	W_M $[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}]$	$G_{\|\|}$ [a.u.]	τ [s]	W_S [kHz]
vTZ/MR_{12}-CISD(20)	0.493	0.01274	2.679	20.0

Latest measurement from JILA group[26]

PT-violating frequency shift $\Delta f = (0.1 \pm 0.87\text{stat} \pm 0.20\text{syst})$ mHz

Using $E_{\text{eff}} = 23.3\ [\frac{\text{GV}}{\text{cm}}] \Rightarrow d_e = (0.9 \pm 7.7\text{stat} \pm 1.7\text{syst}) \times 10^{-29} e$ cm.

Resulting 90% confidence limit: $d_e < 1.3 \times 10^{-28} e$ cm

[25] M. Denis and T. Fleig, (2017) *in preparation*

[26] Private communication (2017), W. Cairncross, J. Ye, E. A. Cornell, *et al.*

TaO^+: Prospective system for EDM measurement[27]

$^{2S+1}\Lambda_\Omega$	$\lambda^o_{n\ell(\omega)_{\text{Atom}}}, \omega = \lvert m_j\rvert, o$: occupation	R_e [a.u.]	ω_e [cm^{-1}]	B_e [cm^{-1}]	T_e [cm^{-1}]
$^3\Delta_1$	88% $\sigma^1_{6s(1/2)_{\text{Ta}}}\delta^1_{5d(3/2)_{\text{Ta}}}$	3.161	1091	0.410	0
$^3\Delta_2$	59% $\sigma^1_{6s(1/2)_{\text{Ta}}}\delta^1_{5d(3/2)_{\text{Ta}}}$, 29% $\sigma^1_{6s(1/2)_{\text{Ta}}}\delta^1_{5d(5/2)_{\text{Ta}}}$	3.160	1092	0.410	1318
$^3\Delta_3$	88% $\sigma^1_{6s(1/2)_{\text{Ta}}}\delta^1_{5d(5/2)_{\text{Ta}}}$	3.160	1093	0.410	3270
$^1\Sigma^+_0$	52% $\sigma^2_{6s(1/2)_{\text{Ta}}}$, 32% $\delta^2_{5d(3/2)_{\text{Ta}}}$, 2% $\delta^2_{5d(5/2)_{\text{Ta}}}$	3.165	1086	0.409	3759
$^3\Sigma^+_0$	12% $\sigma^2_{6s(1/2)_{\text{Ta}}}$, 40% $\delta^2_{5d(3/2)_{\text{Ta}}}$, 35% $\delta^2_{5d(5/2)_{\text{Ta}}}$	3.170	1071	0.408	8265
$^3\Sigma^+_1$	88% $\delta^1_{5d(3/2)_{\text{Ta}}}\delta^1_{5d(5/2)_{\text{Ta}}}$	3.174	1061	0.407	8409
$^1\Delta_2$	27% $\sigma^1_{6s(1/2)_{\text{Ta}}}\delta^1_{5d(3/2)_{\text{Ta}}}$, 57% $\sigma^1_{6s(1/2)_{\text{Ta}}}\delta^1_{5d(5/2)_{\text{Ta}}}$	3.149	1101	0.413	11458

- Combines all advantages of $^3\Delta_1$ molecules
- Electronic ground state is $^3\Delta_1 \Rightarrow$ infinite measurement time

[27] TF, *Phys Rev A* **95** (2017) *022504*

TaO^+

CI Model, R	D [Debye]	E_{eff} $\left[\frac{\text{GV}}{\text{cm}}\right]$	$A_{\|\|}$ [MHz]	W_S [kHz]	W_M $[\frac{10^{33}\text{Hz}}{e\,\text{cm}^2}]$	$G_{\|\|}$ [a.u.]
MR_{12}^{+T}-CISD(10), 3.1 a_0	-3.91	17.6	-4537	15.7	0.38	0.0024
MR_{12}^{+T}-CISD(18), 3.1 a_0	-3.85	20.7	-4593	18.4	0.46	0.0025
MR_{12}^{+T}-CISD(10), 3.1609 a_0	-4.08	17.0	-4492	15.1	0.37	0.0030
MR_{12}^{+T}-CISD(18), 3.1609 a_0	-4.01	20.2	-4544	17.7	0.45	0.0032

Molecular electric dipole moment, EDM effective electric field, magnetic hyperfine interaction constant, scalar-pseudoscalar electron-nucleon interaction constant, nuclear magnetic quadrupole interaction constant and parallel g-tensor component at two internuclear distances R and with two different wavefunction models for the electronic ground state $^3\Delta_1$ ($\Omega = 1$)

- Extremely small magnetic moment in science state
- Favorable ratio $W_d/W_S \Rightarrow$ Potentially stronger constraints

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Malika Denis

LCPQ, Toulouse, France

Malaya K. Nayak

BARC, Mumbai, India

EDMe^-DM